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Graue Glaszusammensetzung
Composition de verre grise

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EP-A- 0 561 337 FR-A- 2 672 587 GB-A- 2 071 082 EP-A- 0 565 882 FR-A- 2 690 437

US-A- 3 296 004

- CHEMICAL ABSTRACTS, vol. 110, no. 20, 15 May 1989, Columbus, Ohio, US; abstract no. 178296d, TOMINAGA MASAHARU ET AL. 'glass for automotive windows' & JP-A-63 277 537 (ASAHI GLASS COMPANY) 15 November 1988
- CHEMICAL ABSTRACTS, vol. 84, no. 16, 19 April 1976, Columbus, Ohio, US; abstract no. 110350f, NAKANO MICHIO ET AL. 'Infrared ray absorbing gray glass' page 314; column R; & JP-A-50 117 810 (NIPPON SHEET GLASS) 16 September 775
- CHEMICAL ABSTRACTS, vol. 108, no. 26, 27
 June 1988, Columbus, Ohio, US; abstract no.
 225789n, ARAYA SHINICHI ET AL.
 'colored-glass compositions for easy
 tempering' page 254; & JP-A-6 340 743
 (CENTRAL GLASS COMPANY) 22 January 1988

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Description

BACKGROUND OF THE INVENTION

[0001] This invention involves a neutral gray colored glass that has a luminous transmittance that makes it highly desirable for use in forward vision areas of a vehicle, such as a windshield and front door windows. In particular, the glass has a luminous transmittance of 70% or greater. In addition, the glass of the present invention generally exhibits lower infrared and total solar energy transmittance comparable to typical green glasses used in automotive applications to reduce heat gain in the interior of the enclosure. The glass is also compatible with flat glass manufacturing methods. [0002] Various heat-absorbing glass substrates are known in the art. The primary colorant in typical green tinted automotive glasses is iron, which is usually present in both the Fe₂O₃ and FeO forms. As is conventional, the total amount of iron present in a glass is expressed herein as Fe₂O₃, regardless of the form actually present. Typical green tinted automotive glass has about 0.5 percent by weight total iron, with the ratio of FeO to total iron being about 0.25. [0003] Some glasses, e.g. U.S. Reissue Patent No. 25,312 to Duncan et al., produce a gray color in the glass by including nickel oxide as a colorant. However, inclusion of nickel containing materials must be carefully controlled because the presence of nickel during the melting process sometimes leads to the formation of nickel sulfide stones in the glass. Additional potential problems faced when using nickel include haze formation on the glass surface due to reduction of the nickel in the tin bath and change in the glass color when it is heat treated.

[0004] To avoid this problem, nickel-free colored glasses containing iron oxide, cobalt oxide, and selenium were developed as disclosed in U.S. Patent No. 3,296,004 to Duncan et al., U.S. Patent No. 3,723,142 to Kato et al. and British Patent Specification 1,331,492 to Bamford. In U.S. Patent No. 4,104,076 to Pons, instead of nickel, Cr_2O_3 or UO_2 are used in combination with iron oxide, cobalt oxide, and selenium to produce gray glass. A more recent, nickel-free version of gray glass is disclosed in U.S. Patent No. 5,023,210 to Krumwiede et al. which uses iron oxide, cobalt oxide, selenium, and chromic oxide as colorants.

[0005] Many of the commercially available gray glasses are too dark to be used in the forward vision area of a vehicle. In addition, the lighter gray glasses exhibit solar performance properties inferior to those of conventional green automotive glass resulting in elevated interior vehicle temperatures which adversely affect occupant comfort. It would be desirable to have a neutral gray glass that may be used for the vision area of a vehicle, have acceptable solar performance properties and further that is compatible with commercial flat glass manufacturing techniques.

SUMMARY OF THE INVENTION

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[0006] The present invention provides a neutral gray colored glass composition having a base glass portion comprising:

SiO ₂	66-75 percent by weight
Na ₂ O	10.20
CaO	5-15
MgO	0-5
Al ₂ O ₃	0-5
K₂O	0-5

and a colorant portion consisting of

0.30 to 0.70 percent by weight
up to 0.19
3-35 ppm
0-10 ppm, or
0.15 to 0.50 percent by weight
up to 0.14
20-30 ppm
0-3 ppm
25-200 ppm

and of optionally an oxide of a material selected from a group consisting of cerium, vanadium, titanium and molybdenum and combination thereof in an amount up to 2.0 wt.% of the glass composition,

and optionally of chromium and manganese as impurities,

the glass having a luminous transmittance as measured using C.I.E. 1931 standard illuminant "A" over the wavelength range 380-770 nm at 10 nm intervals of 70 percent or greater at a thickness of 3.9 millimeters, and a dominant wavelength as measured using C.I.E. 1931 standard illuminant "C" of 485 to 540 nm, with an excitation purity of no higher than 8%.

[0007] A preferred embodiment of such a glass composition includes 0.32 to 0.65 wt. % Fe₂O₃, 0.065 to 0.20 wt. % FeO, 5 to 40 PPM CoO and 1 to 9 PPM Se. In addition, it is preferred that the total solar energy transmittance should be no greater than 65%, and more preferably, no greater than 60%.

[0008] The dominant wavelength of the glasses in the present invention may vary somewhat in accordance with particular color preferences. In the present invention, the glass is a neutral gray color characterized by dominant wavelengths in the range of 480 to 580 nanometers, preferably 485 to 540 nanometers, with an excitation purity of no higher than 8%, preferably no higher than 3%.

DETAILED DESCRIPTION

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[0009] The base glass of the present invention, that is, the major constituents of the glass without colorants, is commercial soda-lime-silica glass characterized as follows:

	Weight %
SiO ₂	66-75
Na ₂ O	10-20
CaO	5-15
MgO	0-5
Al ₂ O ₃	0-5
K ₂ O	0-5
BaO	0-1

[0010] To this base glass the present invention adds colorants in the form of iron, cobalt, selenium and/or nickel. In one particular embodiment of the invention, the glass is essentially nickel-free; that is, no deliberate addition of nickel or nickel compounds is made, although the possibility of traces of nickel due to contamination may not always be avoided. The glass in the present invention is essentially free of other colorants. It should be appreciated that the glass compositions disclosed herein may include small amounts of other materials, for example melting and refining aids, tramp materials or impurities. Such materials may include, but are not limited to chromium, manganese, cerium, molybdenum, titanium, chlorine, zinc, zirconium, sulfur, fluorine, lithium and strontium. It should be further appreciated that some of these materials as well as others may be added to the glass to improve the solar performance of the glass

[0011] The selenium colorant contributes a pink color to the glass as well as a brown color when complexed with as will be discussed later in more detail. iron to form iron selenide (FeSe). Cobalt produces a blue color. Iron contributes yellow and blue in varying proportions depending upon the oxidation state. Nickel, if used, contributes a green-brown to yellow-brown color.

[0012] The glass of the present invention may be melted and refined in a continuous, large-scale, commercial melting operation and formed into flat glass sheets of varying thicknesses by the float method in which the molten glass is supported on a pool of molten metal, usually tin, as it assumes a ribbon shape and is cooled. It should be appreciated that as a result of forming the glass on molten tin, measurable amounts of tin oxide may migrate into surface portions of the glass on the side that was in contact with the tin. Typically, a piece of float glass has an SnO₂ concentration of at least 0.05 wt. % in the first few microns below the surface of the glass that was in contact with the tin.

[0013] The total amount of iron present in the glass is expressed herein in terms of Fe_2O_3 in accordance with standard analytical practice, but that does not imply that all of the iron is actually in the form of Fe₂O₃. Likewise, the amount of iron in the ferrous state is reported as FeO, even though it may not actually be present in the glass as FeO. The proportion of the total iron in the ferrous state is used as a measure of the redox state of the glass and is expressed as the ratio FeO/Fe2O3, which is the weight percent of iron in the ferrous state (expressed as FeO) divided by the weight percent of total iron (expressed as Fe₂O₃). Unless stated otherwise, the term Fe₂O₃ in this specification shall mean total iron expressed in terms of Fe₂O₃ and the term FeO shall mean iron in the ferrous state expressed in terms

[0014] The glass compositions disclosed in the present invention may be made using any of several types of melting arrangements, such as but not limited to, a conventional, overhead fired continuous melting operation as is well known

in the art or a multi-stage melting operation, of the type that is discussed later in more detail. However, for glass compositions having a redox of less than 0.30, the former operation is preferred and for glass compositions having a redox of 0.30 or greater, the latter operation is preferred.

[0015] Conventional, overhead fired continuous melting operations are characterized by depositing batch material onto a pool of molten glass maintained within a tank type melting furnace and applying thermal energy until the materials are melted into the pool of molten glass. The melting tanks conventionally contain a large volume of molten glass so as to provide sufficient residence time for currents in the molten glass to affect some degree of homogenization and fining before the glass is discharged into a forming operation.

[0016] The multi-stage glass melting and refining operation disclosed in U.S. Patent Nos. 4,381,934 and 4,792,536 to Kunkle et al., 4,792,536 to Pecoraro et al. and 4,886,539 to Cerutti et al. is characterized by separate stages whereby more flexibility in controlling redox conditions is provided. The overall melting process disclosed in these patents consists of three stages: a liquefaction stage, a dissolving stage, and a vacuum refining stage. In the liquefaction stage, batch materials, preferably in a pulverulent state, are fed into a rotating, drum-shaped liquefying vessel. As batch material is exposed to the heat within the vessel, liquefied material flows down a sloped batch material lining to a central drain opening at the bottom of the vessel. A stream of liquefied material falls freely from the liquefaction vessel into a dissolving vessel for the dissolving stage. The dissolving vessel completes the dissolution of unmelted particles in the liquefied material coming from the liquefaction stage by providing residence time at a location isolated from the downstream refining stage. The dissolving vessel may be in the form of a horizontally elongated refractory basin with the inlet and outlet at opposite ends thereof so as to assure adequate residence time. The refining stage preferably consists of a vertically upright vessel that may be generally cylindrical in configuration having an interior ceramic refractory lining shrouded in a gas-tight, water-cooled casing. As the molten material enters the vessel from the dissolving vessel, it encounters a reduced pressure within the refining vessel. Gases included in the melt expand in volume, creating a foam. As foam collapses, it is incorporated into the liquid body held in the refining vessel. Refined molten material is drained from the bottom of the refining vessel into a receiving chamber and delivered to a float forming chamber.

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[0017] A stirring arrangement may be employed in the multi-stage process to homogenize the glass after it has been refined in order to produce glass of the highest optical quality. If desired, a stirring arrangement may be integrated with a float forming chamber, whereby the glass in the stirring chamber rests on a layer of molten metal. The molten metal may be continuous with the molten metal constituting the support in the forming chamber, and is usually comprised essentially of tin.

[0018] The multi-stage operation discussed above generally operates at a redox level of 0.30 or higher; however redox levels below 0.30 may be achieved by increasing the amount of oxidizing constituents in the glass batch. For example, manganese oxide may be added to lower the redox level. Redox may also be controlled by adjusting the gas/O₂ ratio of the burners.

[0019] The transmittance data provided throughout this disclosure is based on a glass thickness of 3.9 millimeters (0.154 inch). Luminous transmittance (LTA) is measured using C.I.E. 1931 standard illuminant "A" over the wavelength range 380 to 770 nanometers at 10 nanometer intervals. Total solar ultraviolet transmittance (TSUV) is measured over the wavelength range 300 to 390 nanometers at 10 nanometer intervals. Total solar infrared transmittance (TSIR) is measured over the wavelength range 800 to 2100 nanometers at 50 nanometer intervals. Total solar energy transmittance (TSET) represents a computed value based on measured transmittances from 300 to 2100 nanometers at 50 nanometer intervals. All solar transmittance data is calculated using Parry Moon air mass 2.0 solar data. Glass color in terms of dominant wavelength and excitation purity are measured using C.I.E. 1931 standard illuminant "C" with a 2° observer.

[0020] To determine this transmittance data, the transmittance values are integrated over the wavelength range [a, b]. This range is divided into n equal subintervals of length h by points $\{X_0, X_1, ..., X_n\}$ where $X_i = a + (i \times h)$. In the present disclosure, the Rectangular Rule is used to compute the transmittance data. An interpolating function is used to approximate the integrand f in each subinterval. The sum of integrals of this function provides an approximation of the integral:

$$I = \int_{b}^{a} f(X)dX$$

[0021] In the case of the Rectangular Rule, a constant value $f(X_i)$ is used as an approximation of f(X) on $[X_{i-1}, X_i]$. This yields a step-function approximation of f(X) on [a,b], and the numerical integration formula:

$$1 = \sum_{i=1}^{n} f(X_i) \times h$$

[0022] Tables 1, 2 and 3 illustrate examples of glass compositions at a 3.9 mm (0.154 in.) reference thickness which embody the principles of the present invention. Only the colorant portions of the examples are listed in the table below, with Fe_2O_3 being total iron, including that present as FeO.

[0023] The information provided in Tables 1 and 2 is based on a computer model that generates theoretical spectral properties based on the glass compositions. The compositions in Table 1 exclude nickel oxide as a colorant while the compositions in Table 2 include nickel oxide as a colorant. The information provided in Example 11 of Table 3 is based on an experimental laboratory melt. The remaining information in Table 3 is based on actual glass produced using the multi-stage melting process discussed earlier. However, under certain conditions, it is preferred that the glasses disclosed in the present invention be made using a conventional, overhead fired continuous melting process as discussed earlier.

[0024] It should be noted that the modeled compositions in Table 1 included from 6 to 10 PPM of $\rm Cr_2O_3$ and 1 PPM NiO, both of which are considered to be tramp and/or residual material levels, to better reflect the expected spectral properties of the glass. The compositions in Table 2 included similar $\rm Cr_2O_3$ levels. In addition, the analysis of the experimental melt Example 11 in Table 3 showed less than 3 PPM NiO and 10 PPM $\rm Cr_2O_3$. The analysis of the actual production glass disclosed in Table 3 showed less than 3 PPM NiO and between 5 PPM $\rm Cr_2O_3$.

[0025] The representative base glass composition for the examples is as follows:

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	Examples 1-25	Examples 26-29
SiO ₂	72.8% by weight	72.0% by weight
Na ₂ O	13.8	13.5
CaO	8.8	8.8
MgO	3.8	3.8
Al ₂ O ₃	0.13	0.59

it should be appreciated that this composition may vary especially as a result of the actual amount of colorant present in the glass composition.

TABLE 1

		IADLE	: 1				
Ex.1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
0.570	0.570	0.340	0.570	0.650	0.425	0.650	0.325
0.145	0.145	0.087	0.145	0.195	0.109	0.175	0.065
0.255	0.255	0.255	0.255	0.300	0.255	0.269	0.200
40	40	40	22	20	20	15	32
9	5	7	7	3.5	6	2.5	5
59.67	63.13	65.30	65.57	66.61	69.79		70.02
36.74	36.86	52.76	36.84	27.46	46.32	į	60.63
34.53	37.27	45.99	35.95	39.85			49.67
47.60	49.55	59.20	49.95	45.87	57.39	i	65.50
558.9	493.9	497.4	562.7	493.5	551.3	1	490.6
2.02	2.46	0.39	3.36	3.7	1.3	2.7	1.02
	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	
	0.600	0.425	0.600	0.325	0.425	0.425	
1	0.175	0.128	0.150	0.085	0.108		
	0.292	0.167 0.300	0.250	0.262	0.255		1
	15	20	15	25	20	20	
	2.5	3.5	2.5	4.5	1	1	
	70.10	71.12	71.31	71.48	1		
ļ	30.97	41.27	36.01				•
	42.05	48.81	40.56	1]
	49.30	55.68	52.38	1	1		1
	494.9	491.7	501.7		1	1	
Į.	3.2	2.58	1.97	1.41	1.58	1 3.46	1
	0.570 0.145 0.255 40 9 59.67 36.74 34.53 47.60 558.9	0.570	Ex.1 Ex. 2 Ex. 3 0.570 0.570 0.340 0.145 0.145 0.087 0.255 0.255 0.255 40 40 40 9 5 7 59.67 63.13 65.30 36.74 36.86 52.76 34.53 37.27 45.99 47.60 49.55 59.20 558.9 493.9 497.4 2.02 2.46 0.39 Ex. 2 Ex. 3 0.600 0.425 0.175 0.128 0.292 0.167 0.300 15 20 2.5 3.5 70.10 71.12 30.97 41.27 42.05 48.81 49.30 55.68 494.9 491.7	Ex.1 Ex. 2 Ex. 3 Ex. 4 0.570 0.570 0.340 0.570 0.145 0.087 0.145 0.255 0.255 0.255 40 40 40 22 7 7 59.67 63.13 65.30 65.57 36.74 36.86 52.76 36.84 34.53 37.27 45.99 35.95 47.60 49.55 59.20 49.95 558.9 493.9 497.4 562.7 2.02 2.46 0.39 3.36 Ex. 2 Ex. 3 Ex. 4 0.600 0.425 0.600 0.175 0.128 0.150 0.292 0.167 0.300 0.250 15 20 15 2.5 70.10 71.12 71.31 30.97 41.27 36.01 42.05 48.81 40.56 49.30 55.68 52.38 <t< td=""><td>0.570 0.570 0.340 0.570 0.650 0.145 0.145 0.087 0.145 0.195 0.255 0.255 0.255 0.300 40 40 40 22 20 9 5 7 7 3.5 59.67 63.13 65.30 65.57 66.61 36.74 36.86 52.76 36.84 27.46 34.53 37.27 45.99 35.95 39.85 47.60 49.55 59.20 49.95 45.87 558.9 493.9 497.4 562.7 493.5 2.02 2.46 0.39 3.36 3.7 Ex. 2 Ex. 3 Ex. 4 Ex. 5 0.600 0.425 0.600 0.325 0.175 0.128 0.150 0.085 0.292 0.167 0.300 0.250 0.262 15 20 15 25 2.5 3.5 2.5 <td< td=""><td>Ex.1 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 0.570 0.570 0.340 0.570 0.650 0.425 0.145 0.145 0.087 0.145 0.195 0.109 0.255 0.255 0.255 0.300 0.255 40 40 40 22 20 20 9 5 7 7 3.5 6 59.67 63.13 65.30 65.57 66.61 69.79 36.74 36.86 52.76 36.84 27.46 46.32 34.53 37.27 45.99 35.95 39.85 45.43 47.60 49.55 59.20 49.95 45.87 57.39 558.9 493.9 497.4 562.7 493.5 551.3 2.02 2.46 0.39 3.36 3.7 1.3 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 0.600 0.425 0.600 0.325</td></td<></td></t<> <td>Ex.1 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 Ex. 7 0.570 0.570 0.340 0.570 0.650 0.425 0.650 0.145 0.145 0.195 0.109 0.175 0.255 0.255 0.255 0.300 0.255 0.269 40 40 40 22 20 20 15 9 5 7 7 3.5 6 2.5 59.67 63.13 65.30 65.57 66.61 69.79 69.80 36.74 36.86 52.76 36.84 27.46 46.32 30.97 34.53 37.27 45.99 35.95 39.85 45.43 39.42 47.60 49.55 59.20 49.95 45.87 57.39 48.99 558.9 493.9 497.4 562.7 493.5 551.3 498.1 2.02 2.46 0.39 3.36 3.7 1.3 2.7</td>	0.570 0.570 0.340 0.570 0.650 0.145 0.145 0.087 0.145 0.195 0.255 0.255 0.255 0.300 40 40 40 22 20 9 5 7 7 3.5 59.67 63.13 65.30 65.57 66.61 36.74 36.86 52.76 36.84 27.46 34.53 37.27 45.99 35.95 39.85 47.60 49.55 59.20 49.95 45.87 558.9 493.9 497.4 562.7 493.5 2.02 2.46 0.39 3.36 3.7 Ex. 2 Ex. 3 Ex. 4 Ex. 5 0.600 0.425 0.600 0.325 0.175 0.128 0.150 0.085 0.292 0.167 0.300 0.250 0.262 15 20 15 25 2.5 3.5 2.5 <td< td=""><td>Ex.1 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 0.570 0.570 0.340 0.570 0.650 0.425 0.145 0.145 0.087 0.145 0.195 0.109 0.255 0.255 0.255 0.300 0.255 40 40 40 22 20 20 9 5 7 7 3.5 6 59.67 63.13 65.30 65.57 66.61 69.79 36.74 36.86 52.76 36.84 27.46 46.32 34.53 37.27 45.99 35.95 39.85 45.43 47.60 49.55 59.20 49.95 45.87 57.39 558.9 493.9 497.4 562.7 493.5 551.3 2.02 2.46 0.39 3.36 3.7 1.3 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 0.600 0.425 0.600 0.325</td></td<>	Ex.1 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 0.570 0.570 0.340 0.570 0.650 0.425 0.145 0.145 0.087 0.145 0.195 0.109 0.255 0.255 0.255 0.300 0.255 40 40 40 22 20 20 9 5 7 7 3.5 6 59.67 63.13 65.30 65.57 66.61 69.79 36.74 36.86 52.76 36.84 27.46 46.32 34.53 37.27 45.99 35.95 39.85 45.43 47.60 49.55 59.20 49.95 45.87 57.39 558.9 493.9 497.4 562.7 493.5 551.3 2.02 2.46 0.39 3.36 3.7 1.3 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 0.600 0.425 0.600 0.325	Ex.1 Ex. 2 Ex. 3 Ex. 4 Ex. 5 Ex. 6 Ex. 7 0.570 0.570 0.340 0.570 0.650 0.425 0.650 0.145 0.145 0.195 0.109 0.175 0.255 0.255 0.255 0.300 0.255 0.269 40 40 40 22 20 20 15 9 5 7 7 3.5 6 2.5 59.67 63.13 65.30 65.57 66.61 69.79 69.80 36.74 36.86 52.76 36.84 27.46 46.32 30.97 34.53 37.27 45.99 35.95 39.85 45.43 39.42 47.60 49.55 59.20 49.95 45.87 57.39 48.99 558.9 493.9 497.4 562.7 493.5 551.3 498.1 2.02 2.46 0.39 3.36 3.7 1.3 2.7

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TABLE 2

	Ex. 8	Ex.9	Ex. 10
Fe ₂ O ₃ wt.%	0.425	0.200	0.300
FeO wt. %	0.108	0.051	0.077
Redox	0.255	0.255	0.255
C ₀ O PPM	22	27	22
Se PPM	0	0	0.5
NiO PPM	100	150	100
LTA	70.31	70.86	72.19
TSIR	46.01	65.42	56.06
TSUV	50.00	63.80	56.60
TSET	57.95	68.96	64.29
DW nm	497.5	498.0	498.0
Pe %	2.29	1.26	1.55

TABLE 3

	Ex. 11	Ex. 12	Ex. 13	Ex. 14
Fe ₂ O ₃ wt.%	0.432	0.377	0.371	0.415
FeO wt. %	0.109	0.107	0.107	0.111
Redox	0.252	0.283	0.289	0.268
CoO PPM	19	19	23	18
Se PPM	5	4	3	3
LTA	70.87	72.3	72.49	72.94
TSIR	46.53	47.50	47.45	46.25
TSUV	49.98	51.64	53.67	51.49
TSET	58.09	59.61	60.01	59.33
DW nm	532.9	500.2	488.6	493.7
Pe %	0.97	0.85	2.47	1.54

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[0026] Referring to Tables 1, 2 and 3, the present invention provides a neutral gray colored glass using a standard soda-lime-silica glass base composition and iron, cobalt, selenium and/or nickel as colorants. Not all of the examples are the same gray color as indicated by the dominant wavelengths (DW) and excitation purities (Pe). In the present invention, the glass has a neutral gray color characterized by dominant wavelengths in the range of 485 to 540 nanometers, with an excitation purity of no higher than 8%, preferably no higher than 3%.

[0027] An alternate embodiment of the invention further includes nickel oxide as a colorant. In particular, it has also been found that a neutral gray colored glass with a luminous transmittance of 60% and higher at a thickness of 3.9 millimeters may be attained by using 0.15 to 0.65 wt. % Fe₂O₃, no greater than 0.18 wt. % FeO, 15-55 PPM CoO, O-5 PPM Se and 25-350 PPM NiO as colorants. A preferred embodiment of this alternate glass composition includes 0.17 to 0.60 wt. % Fe₂O₃, 0.04 to 0.16 wt. % FeO, 20 to 52 PPM CoO, 0 to 3 PPM Se and at least 50 PPM NiO.

[0028] The redox ratio for the glass of the present invention is preferably maintained between about 0.20 to 0.30, and more preferably between 0.24 to 0.28 which is the typical operating range for a conventional overhead fired melting operation. Higher redox levels may be attained by processes disclosed herein, but the use of higher redox ratios is preferably avoided to prevent excessive volatilization of selenium during melting.

[0029] Glass made by the float process typically ranges from a sheet thickness of about 1 millimeters to 10 millimeters. For the vehicle glazing applications, it is preferred that the glass sheets have a thickness within the thickness range of 1.8 to 6 millimeters.

[0030] If desired, ultraviolet radiation absorbing materials may be added to the glass compositions of the present invention to improve its solar performance. Although not limiting in the present invention, a total of up to 2.0 wt. % of oxides of cerium, vanadium, titanium and molybdenum and combinations thereof may be used as UV absorbers to reduce the TSUV of the glass. In a preferred embodiment of the invention, TiO₂ is the preferred UV absorber and may be added in an amount ranging from 0.1 to 1.0 wt. % of the glass composition, and more preferably 0.2 to 0.5 wt. %. [0031] In general, when the glass is used in a forward vision area of a vehicle, it is required that the LTA be 70% or

greater. When the required LTA is 70% or greater, the colorants used to produce the nickel-free neutral gray glass of the present invention include 0.30 to 0.70 wt. % Fe_2O_3 , up to 0.19 wt. % FeO, 3 to 35 PPM CoO and 0 to 10 PPM Se, and preferably 0.32 to 0.65 wt. % Fe_2O_3 , 0.065 to 0.175 wt. % FeO, 5 to 32 PPM CoO and 1 to 5 PPM Se. The colorants to produce a luminous transmittance of 70% and greater for in the alternate neutral gray glass composition which includes nickel oxide as a colorant include 0.15 to 0.50 wt. % Fe_2O_3 , up to 0.14 wt. % FeO, 20 to 30 PPM CoO, 0 to 3 PPM Se and 25-200 PPM NiO, and preferably 0.20 to 0.43 wt. % Fe_2O_3 , 0.05 to 0.11 wt. % FeO, 22 to 27 PPM CoO, 0 to 2 PPM Se and at least 50 PPM NiO.

[0032] In addition, for a forward vision area application, it is preferred that the glass composition provide a total solar energy transmittance of no greater than 65%, and more preferably no greater than 60%. This type of performance would make the glass comparable to the performance of standard green automotive glasses.

[0033] Other variations as are known to those of skill in the art may be resorted to without departing from the scope of the invention as defined by the claims that follow.

5 Claims

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1. A neutral gray colored glass composition having a base glass portion comprising:

SiO ₂	66-75 percent by weight
Na ₂ O	10-20
CaO	5-15
MgO	0-5
Al ₂ O ₃	0-5
K ₂ O	0-5

and a colorant portion consisiting of

Fe ₂ O ₃ (total iron)	0.30 to 0.70 percent by weight
FeO	up to 0.19
C ₀ O	3-35 ppm
Se	0-10 ppm, or
Fe ₂ O ₃ (total iron)	0.15 to 0.50 percent by weight
FeO	up to 0.14
CoO	20-30 ppm
Se	0-3 ppm
NiO	25-200 ppm

and of optionally an oxide of a material selected from a group consisting of cerium, vanadium, titanium and molybdenum and combination thereof in an amount up to 2.0, wt.% of the glass composition, and optionally of chromium and manganese as impurities,

the glass having a luminous transmittance as measured using C.I.E. 1931 standard illuminant "A" over the wavelength range 380-770 nm at 10 nm intervals of 70 percent. or greater at a thickness of 3.9 millimeters, and a dominant wavelength as measured using C.I.E. 1931 standard illuminant "C" of 485 to 540 nm, with an excitation purity of no higher than 8%.

- The composition as in claim 1 wherein the Fe₂O₃ concentration is from 0.32 to 0.65 weight percent, the FeO concentration is from 0.065 to 0.175 weight percent, the Co0 concentration is from 5 to 32 ppm and the Se concentration is from 1 to 5 ppm.
- 3. The composition as in claim 1 wherein the Fe_2O_3 concentration is from 0.20 to 0.43 weight percent, the FeO concentration is from 0.05 to 0.11 weight percent, the CoO concentration is from 22 to 27 ppm, the Se concentration is from 0 to 2 ppm and the NiO concentration is at least 50 ppm.
- 4. The composition of any of claims 1-3 wherein the color of the glass is characterized by an excitation purity of no higher than 3%.

- The composition as in any of claims 1-4 wherein said TiO₂ is in an amount from 0.1 to 1.0 wt,%.
- A glass sheet made from the composition as recited in claims 1 to 5.
- 7. The glass sheet as in claim 6 wherein the sheet has a thickness between 1.8 to 6 mm.

Patentansprüche

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Eine neutral grau gefärbte Glaszusammensetzung mit einem Basisglasanteil enthaltend:

SiO ₂	66-75 Gew%
Na ₂ O	10-20
CaO	5-15
MgO	0-5
Al ₂ O ₃	0-5
K ₂ O	0-5

20 und einen Färbungsmittelanteil bestehend aus

	Fe ₂ O ₃ (Gesamteisen)	0,30 bis 0,70 Gew%
	FeO	bis zu 0,19
	CoO	3-35 ppm
	Se	0-10 ppm, oder
	Fe ₂ O ₃ (Gesamteisen)	0,15 bis 0,50 Gew%
	FeO	bis zu 0,14
	CoO	20-30 ppm
	Se	0-3 ppm
l	NiO	25-200 ppm

und aus gegebenenfalls einem Oxid eines Materials ausgewählt aus einer Gruppe bestehend aus Cer, Vanadium, Titan und Molybdän und Kombinationen davon in einer Menge von bis zu 2,0 Gew.-% der Glaszusammensetzung, und gegebenenfalls aus Chrom und Mangan als Verunreinigung, wobei das Glas eine Durchlässigkeit im sichtbaren Bereich gemessen unter Verwendung von C.I.E. 1931 Standard Illuminant "A" über den Wellenlängenbereich 380-770 nm bei 10 nm-Intervallen von 70% oder größer bei einer Dicke von 3,9 mm und eine dominante Wellenlänge gemessen unter Verwendung von C.I.E. 1931 Standard Illuminant "C" von 485 bis 540 nm bei einer Anregungsreinheit von nicht mehr als 8% aufweist.

- Zusammensetzung wie in Anspruch 1, wobei die Fe₂O₃-Konzentration 0,32 bis 0,65 Gew.-% beträgt, die FeO-Konzentration 0,065 bis 0,175 Gew.-% beträgt, die CoO-Konzentration 5 bis 32 ppm beträgt und die Se-Konzentration 1 bis 5 ppm beträgt.
- 3. Zusammensetzung wie in Anspruch 1, wobei die Fe_{2O3}-Konzentration 0,20 bis 0,43 Gew.-% beträgt, die Fe0-Konzentration 0,05 bis 0,11 Gew.-% beträgt, die CoO-Konzentration 22 bis 27 ppm beträgt, die Se-Konzentration 0 bis 2 ppm beträgt und die Ni-Konzentration wenigstens 50 ppm beträgt.
 - 4. Zusammensetzung nach einem der Ansprüche 1-3, wobei die Farbe des Glases durch eine Anregungsreinheit von nicht höher als 3% charakterisiert ist.
 - Zusammensetzung nach einem der Ansprüche 1-4, worin dieses TiO₂ in einer Menge von 0,1 bis 1,0 Gew.-% vorhanden ist.
- Glasscheibe, die aus der Zusammensetzung wie in Ansprüchen 1-5 definiert hergestellt ist.
 - 7. Glasscheibe wie in Anspruch 6, wobei die Scheibe eine Dicke zwischen 1,8 bis 6 mm hat.

Revendications

1. Composition de verre de couleur grise neutre comportant une partie de verre de base comprenant :

SiO ₂	66 - 75% en poids
Na ₂ O	10 - 20% en poids
CaO	5 - 15% en poids
MgO	0 - 5% en poids
Al ₂ O ₃	0 - 5% en poids
K ₂ O	0 - 5% en poids

et une partie colorante se composant de

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Fe₂O₃ (fer total) 0,30 à 0,70% en poids FeO jusqu'à 0,19% en poids CoO 3 - 35 ppm Se 0 -10 ppm, ou Fe₂O₃ (fer total) 0,15 à 0,50% en poids FeO jusqu'à 0,14% en poids CoO 20 - 30 ppm Se 0 - 3 ppm NiO 25 - 200 ppm

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et d'éventuellement un oxyde d'une matière choisie dans le groupe comprenant le cérium, le vanadium, le titane et le molybdène et leurs combinaisons en une quantité allant jusqu'à 2,0% en poids de la composition de verre,

et éventuellement du chrome et du manganèse comme impuretés,

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le verre ayant une transmission lumineuse telle que mesurée en utilisant une source de lumière "A" standard C.I.E. 1931 sur la gamme de longueurs d'onde de 380-770 nm à des intervalles de 10 nm de 70% ou plus à une épaisseur de 3,9 mm, et une longueur d'onde dominante telle que mesurée en utilisant une source de lumière "C" standard C.I.E. 1931 de 485 à 540 nm, avec une pureté d'excitation de pas plus de 8%.

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- 2. Composition suivant la revendication 1, dans laquelle la concentration en Fe₂O₃ est de 0,32 à 0,65% en poids, la concentration en FeO est de 0,065 à 0,175% en poids, la concentration en CoO est de 5 à 32 ppm et la concentration en Se est de 1 à 5 ppm.
- Composition suivant la revendication 1, dans laquelle la concentration en Fe₂O₃ est de 0,20 à 0,43% en poids, la concentration en FeO est de 0,05 à 0,11% en poids, la concentration en CoO est de 22 à 27 ppm, la concentration en Se est de 0 à 2 ppm et la concentration en NiO est d'au moins 50 ppm.
 - 4. Composition suivant l'une quelconque des revendications 1 à 3, dans laquelle la couleur du verre est caractérisée par une pureté d'excitation de pas plus de 3%.

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- Composition suivant l'une quelconque des revendications 1 à 4, dans laquelle le TiO₂ précité est en une quantité de 0,1 à 1,0% en poids.
- 6. Feuille de verre faite de la composition suivant l'une quelconque des revendications 1 à 5.

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7. Feuille de verre suivant la revendication 6, dans laquelle la feuille a une épaisseur entre 1,8 et 6 mm.

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